



CIS film growth by metallic ink coating and selenization

G. Norsworthy^{a,*}, C.R. Leidholm^a, A. Halani^a, V.K. Kapur^a,
R. Roe^a, B.M. Basol^a, R. Matson^b

^aInternational Solar Electric Technology Inc. (ISET), 8635 Aviation Blvd., Inglewood, CA 90301, USA

^bNREL, 1617 Cole Blvd., Golden, CO 80401, USA

Abstract

A novel technique was demonstrated for the growth of CuInSe₂ (CIS) thin films. The technique used an ink formulation containing sub-micron size particles of Cu–In alloys. A metallic precursor layer was first formed by coating this ink onto the substrate by spraying. The precursor film was then made to react with Se to form the CIS compound. The morphology of the CIS layers depended on the initial composition of the Cu–In particles as well as the post-deposition treatments. Solar cells were fabricated on CIS absorber layers prepared by this low-cost ink-coating approach and devices with a conversion efficiency of over 10.5% were demonstrated. © 2000 Elsevier Science B.V. All rights reserved.

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1. Introduction

High-efficiency polycrystalline thin-film solar cells have commonly been fabricated on CuInSe₂ (CIS) or Cu(In,Ga)Se₂ (CIGS) absorber layers deposited by vacuum deposition techniques such as evaporation [1] and two-stage processes utilizing evaporated or sputter deposited precursors [2]. There is presently great interest in the development of low-cost processing methods for the growth of high-quality CIS-type absorbers for thin film solar cell applications. Among the low-cost approaches investigated are electrodeposition [3] and a group of techniques that are based on “particle deposition” [4].

* Corresponding author. Tel.: 310-6609680; fax: 310-2162908.

Slurry or ink deposition by large-area non-vacuum coating methods such as screen printing, spraying, curtain coating, roll coating or doctor blading are attractive low-cost approaches for the growth of thin film solar cell absorbers, provided that the precursor layers obtained by these particle deposition techniques can be successfully converted into high-quality semiconductor layers.

There have been several attempts to obtain solar-cell-grade CIS absorbers using the screen printing technique. In these attempts, powders and liquid media were mixed and ball-milling utilized for particle size reduction and paste formation. For example, Arita et al. manufactured a screen printable paste using ball-milled Cu, In and Se powders [5]. Other groups used paste compositions that contained CIS powder, Se and fluxing agents such as Cu_xSe and CuTlSe_2 [6,7]. After screen printing, the precursor layers were annealed at high temperatures ($> 600^\circ\text{C}$) to convert them into well-fused polycrystalline CIS films. The efficiencies of solar cells fabricated on absorbers grown by the above-mentioned screen printing techniques, however, were well below 5%. An attempt to prepare a screen printable paste out of a mixture of Cu and In powders did not yield good results because of poor paste quality [8]. More recently, nano-size particles were employed in ink formulations that did not require mechanical milling and particle size reduction. For example, Schultz et al. sprayed inks containing CIS, or Cu–Se and In–Se nano-particle species onto heated substrates for CIS growth [9]. Efficient solar cells were reported on films grown by a nano-particle deposition technique, details of which were not given [10]. Recently, we developed a new ink-coating technique that was successfully employed for the growth of CIS absorbers that were used for the fabrication of over 9% efficient thin film solar cells [11]. In this paper we present details of this processing approach that yielded better than 10% efficient solar cells.

2. Experimental

The processing technique used in this work included the steps of: (i) preparing a metallic powder containing Cu–In alloys, (ii) forming an ink using this powder, (iii) depositing the ink over a substrate in the form of a thin precursor layer, and finally, (iv) annealing the metallic precursor layer in a Se atmosphere at high temperature to form the CIS compound [4,11].

The metallic powders used in this work contained Cu–In alloys obtained by the melt atomization technique. To prepare the powders, 99.99% pure Cu and In were melted under a hydrogen curtain at a temperature above 900°C . The Cu/In ratio of the melt was fixed at the targeted values of 0.88, 0.98, and 1.05. The liquid alloys were transformed into powder form in a gas atomizer employing Ar as the quenching gas. The powder was sieved to remove particles larger than approximately $20\ \mu\text{m}$.

About 10 g of the sieved Cu–In powder was mixed with 23 g of water. A small amount (about 1.5% by weight) of a wetting agent and a dispersant were added to this aqueous formulation. The mixture was milled in a ball mill to form an ink. Glass/Mo substrates were prepared by depositing $0.5\text{--}3.0\ \mu\text{m}$ thick Mo layers on 3 mm thick soda-lime glass sheets in an in-line DC magnetron sputtering system. Precursor films

containing the milled Cu–In alloy pigment were coated over glass or glass/Mo substrates by spraying. After coating, the wet films were dried in an oven at 60°C for one minute.

Selenization of the precursor layers was carried out in a reactor that employed a 5% H₂Se + 95% N₂ gas mixture. The selenization temperature was 440°C and the selenization time 30 min.

Solar cells with the glass/Mo/CIS/CdZnS/ZnO structure were fabricated on the CIS absorbers by depositing CdZnS buffer layers and ZnO window films as discussed in Ref. [11]. Device measurements were carried out under an ELH lamp solar simulator calibrated to AM 1.5 using a CIS reference cell.

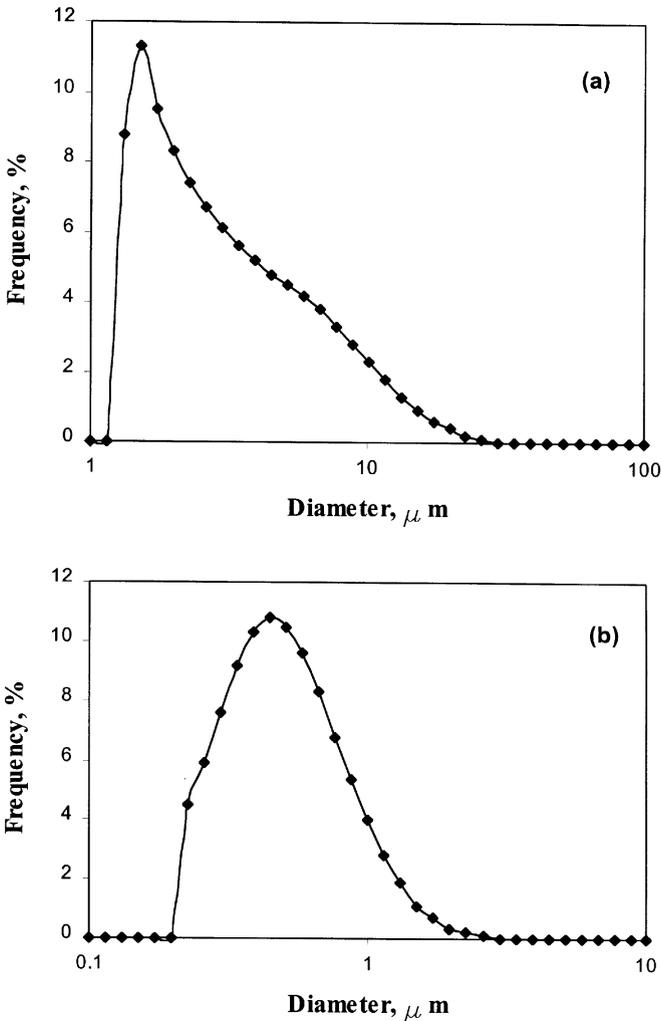


Fig. 1. Particle size distribution of (a) starting sieved powder, (b) powder in the milled ink.

3. Results and discussion

A unique feature of the present method is the use of powders of Cu–In alloys in the ink formulation. These alloys are more brittle than the individual elements and therefore can be efficiently milled for particle size reduction and ink formation. Fig. 1 shows the particle size distribution of the starting powder after sieving and in the milled ink, respectively. The frequency was calculated according to the number distribution mode. The mean particle size of the starting powder was found to be $3.74\ \mu\text{m}$ and the mean particle size in the milled ink was $0.53\ \mu\text{m}$, clearly demonstrating the particle size reduction. It should be noted that previous attempts to mill Cu and In powders [8] did not yield good results. This is not surprising because In is a soft metal and cannot be effectively milled.

In-depth characterization of the phases present in the starting powders and the precursor layers was previously carried out [4]. In summary, the starting powders obtained by the melt atomization technique were found to contain Cu-rich phases of Cu_9In_4 and Cu_2In and In-rich phase of CuIn_2 in addition to pure In. Upon milling and ink formation, the phase content changed into $\text{Cu}_{11}\text{In}_9 + \text{CuIn}_2$ due to the mechanical alloying of the pure In phase with the highly Cu-rich phases. Therefore, the precursor layers selenized in this study originally contained $\text{Cu}_{11}\text{In}_9$ and CuIn_2 phases. Upon heating over 150°C the CuIn_2 phase disappeared and the phase composition changed to $\text{Cu}_{11}\text{In}_9 + \text{In}$.

The cross-sectional SEM shown in Fig. 2 was taken from a precursor film that was spray-deposited on a glass/Mo substrate. The average thickness of this precursor layer

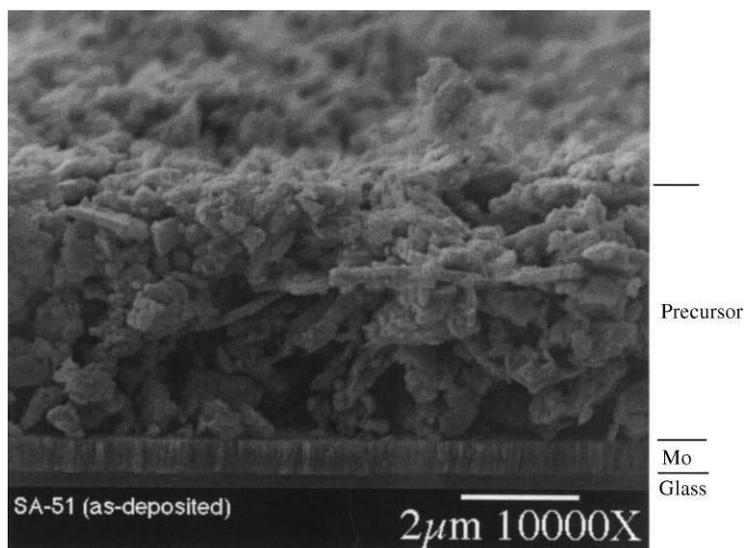


Fig. 2. Cross-sectional SEM of a precursor layer spray deposited on a Mo/glass substrate, taken at $\sim 80^\circ$ tilt to reveal both the cross section of the film and some of the corresponding surface.

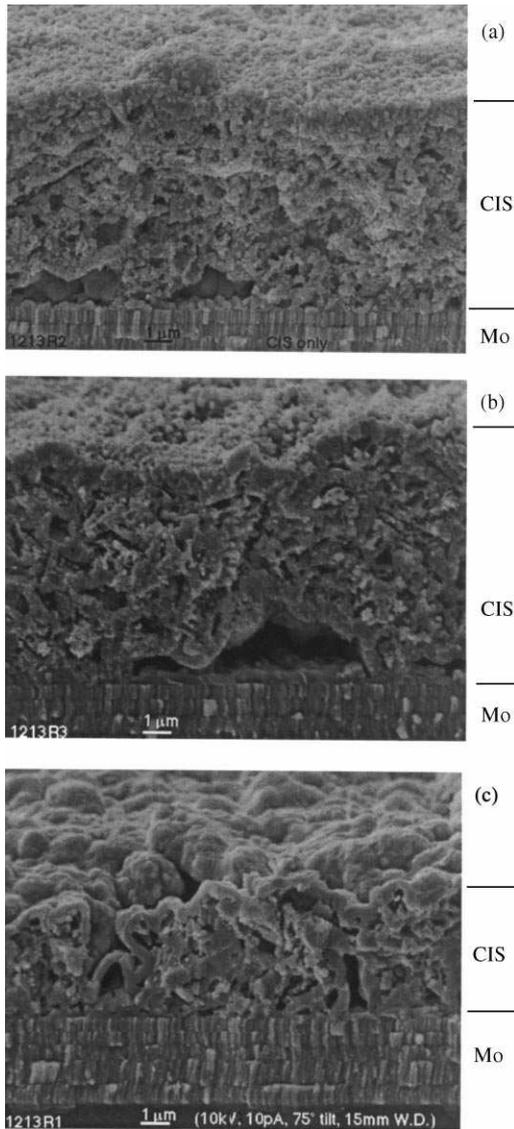


Fig. 3. Cross-sectional SEMs of CIS/Mo/glass structures obtained by the selenization of precursor films with: (a) $\text{Cu/In} = 0.88$, (b) $\text{Cu/In} = 0.98$, (c) $\text{Cu/In} = 1.05$. Micrographs were taken at $\sim 80^\circ$ tilt to reveal both the cross section of the film and some of the corresponding surface.

is about $4 \mu\text{m}$. The alloy particles forming the film are randomly shaped. There are sub-micron size particles as well as thin platelets that are as long as $2 \mu\text{m}$. It should be noted that these platelets formed as the original round particles broke under the action of the heavy ceramic balls during the milling step. Since the particles forming the precursor layer of Fig. 2 are randomly shaped, their packing density is rather low.

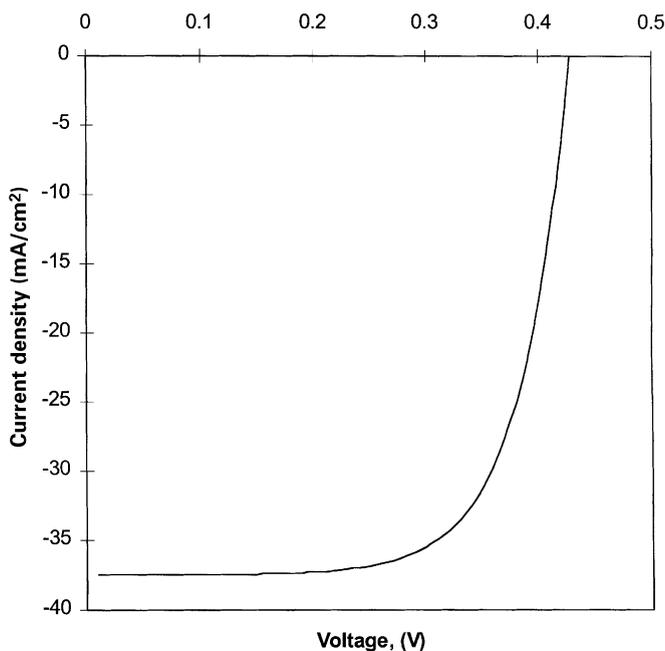


Fig. 4. Illuminated I - V characteristics of a solar cell fabricated on a CIS absorber. Area = 0.1 cm^2 , $\eta = 10.56\%$, $V_{oc} = 0.43 \text{ V}$, $J_{sc} = 37.5 \text{ mA/cm}^2$ and $FF = 65.5\%$.

The microstructure of the CIS layers formed by the selenization of the precursor layers, such as the one depicted in Fig. 2, was found to depend on the composition of the starting powder. Fig. 3 shows the cross-sectional SEMs taken from CIS layers grown using inks with overall Cu/In ratios of 0.88, 0.98 and 1.05. In all cases, the crust of the film is well fused and dense, but the bulk is porous. There is no clear grain structure that can be observed in the film with a Cu/In ratio of 0.88. The film with the Cu/In ratio of 0.98 has a visible network of consolidated regions, whereas filamentary grains of $> 1 \mu\text{m}$ can be observed around the voids in the Cu-rich absorber layer. Grain growth in the Cu-rich CIS layers is due to the presence of excess CuSe phase with a low melting point.

The relatively porous films, such as the ones shown in Fig. 3, were successfully used to demonstrate high-efficiency solar cells with conversion efficiencies in the range of 10–11%. The well-fused, dense crust on the surfaces of these layers was adequate to make these devices active. Fig. 4 shows the illuminated I - V characteristics of a device fabricated on an absorber with Cu/In ratio of 0.88. The efficiency of this 0.1 cm^2 area device is 10.56% with the open circuit voltage (V_{oc}), short circuit current density (J_{sc}) and fill factor (FF) values of 0.43 V, 37.5 mA/cm^2 and 65.5%, respectively.

Densification studies were initiated to improve the grain size and the morphology of the CIS layers grown by the ink spraying technique. Fig. 5 shows an SEM of a selenized film which was compressed before the selenization step using a 3 cm

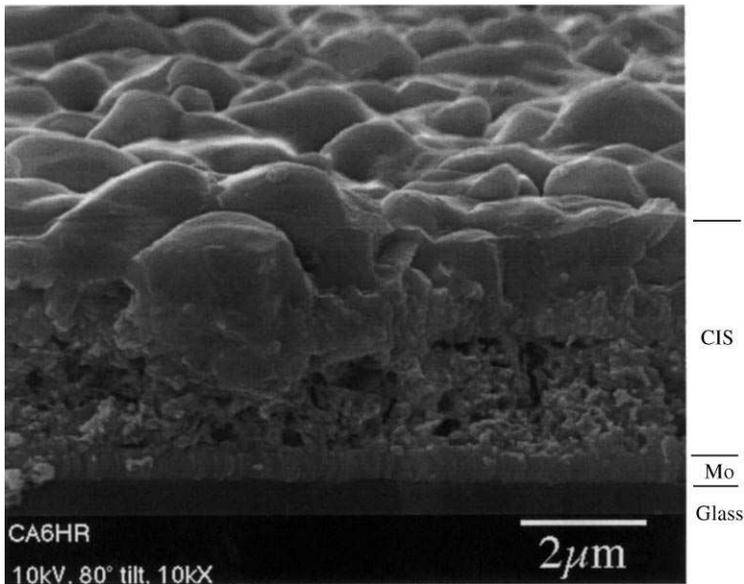


Fig. 5. Cross-sectional SEM of a CIS film on a Mo/glass substrate. The precursor film was compressed after spray deposition and then selenized.

diameter polished stainless-steel ball race in an attempt to obtain a denser film. The pressure was estimated to be 7×10^4 kN/m², resulting in a reduction in the thickness of the precursor film from 3.7 to 2.5 μm . The dense crystals forming a crust on the selenized film are approximately 50% of the thickness of the film compared to approximately 15% of the film which was not pressed. Further densification studies as well as work on devices fabricated on densified layers are in progress.

4. Conclusions

A truly low-cost technique was demonstrated for the growth of CIS-type compound semiconductors. In this method, a metallic ink containing Groups I and III elements was first formed and deposited on the selected substrate, then a selenization step converted the metallic precursor into the desired selenide compound. This technique is applicable to the growth of films containing Ga and/or S also.

Non-vacuum techniques based on nano-particle deposition, such as the one described in this paper, are desirable for CIS-type solar cell manufacturing because these techniques offer the possibility of low-cost processing. There is a wide range of particle-based techniques that can be applied to the deposition of precursors containing Groups I and III materials onto large-area substrates. For example, starting powders consisting of nano-particles can be employed as the source material in a plasma spraying approach to deposit precursor layers directly on the substrate.

These precursors can then be converted into well-fused Group I–III–VI₂ compound layers. In the case of metallic powders, pure Groups I and III nanopowders can be included in an ink or paste formulation without the use of mechanical milling and then this formulation can be deposited onto the selected substrates through spraying, doctor blading, screen printing, etc. In all of these approaches care needs to be taken to grow compound layers with high density and good morphology.

Acknowledgements

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References

- [1] J.R. Tuttle, M.A. Contreras, K.R. Ramanathan, S.E. Asher, B. Bhattacharya, T.A. Berens, J. Keane, R. Noufi, NREL/SNL Photovoltaics Program Review, November 1996, in: C.E. Witt, M. Al-Jassim, J.M. Gee (Eds.), AIP Conference Proceedings 394. American Institute of Physics, Woodbury, NY, 1997, p. 83.
- [2] B.M. Başol, Preparation techniques for thin film solar cell materials: processing perspectives, *Jpn. J. Appl. Phys.* 32 (1993) 35.
- [3] R.N. Bhattacharya, W. Batchelor, J.E. Granata, F. Hasoon, H. Wiesner, R. Ramanathan, J. Keane, R. Noufi, CuIn_{1-x}Ga_xSe₂-based photovoltaic cells from electrodeposited, chemical bath deposited precursors, *Sol. Energy Mater. Sol. Cells* 55 (1998) 83.
- [4] B.M. Başol, Low cost techniques for the preparation of CIGSS absorber layers, Proceedings of the European MRS Conference, June 1–4, 1999, Strasbourg, France, in press.
- [5] T. Arita, N. Suyama, Y. Kita, S. Kitamura, T. Hibino, H. Takada, K. Omura, N. Ueno, M. Murozono, CuInSe₂ films prepared by screen-printing, and sintering method, Proceedings of the 20th IEEE Photovoltaic Specialists Conference, IEEE, New York, 1988, p. 1650
- [6] A. Vervaet, M. Burgelman, I. Clemminck, J. Capon, Screen printing of CuInSe₂ films, Proceedings of the Ninth EC Photovoltaic Solar Energy Conference, 1989, p. 480.
- [7] M. Casteleyn, M. Burgelman, B. Depuydt, I. Clemminck, Growth studies of CuInSe₂ using Cu–Se fluxes, Proceedings of the 12th EC Photovoltaic Solar Energy Conference, 1994, 604.
- [8] A. Vervaet, M. Burgelman, I. Clemminck, M. Casteleyn, Screen printing of CIS for CIS–CdS solar cells, Proceedings of the 10th EC Photovoltaic Solar Energy Conference, 1991, p. 900.
- [9] D.L. Schulz, C.J. Curtis, A. Cram, J.L. Alleman, A. Mason, R.J. Matson, J.D. Perkins, D.S. Ginley, CIGS films via nanoparticle spray deposition: attempts at densifying a porous precursor, Proceedings of the 26th IEEE Photovoltaic Specialists Conference, IEEE, New York, 1997, p. 483.
- [10] C. Eberspacher, K.L. Pauls, C.V. Fredric, Improved processes for forming CuInSe₂ films, Proceedings of the second World Conference on Photovoltaic Solar Energy Conversion, 1998, p. 303.
- [11] B.M. Başol, V.K. Kapur, G. Norsworthy, A. Halani, C.R. Leidholm, R. Roe, Efficient CuInSe₂ solar cells fabricated by a novel ink coating approach, *Electrochem. Solid State Lett.* 1 (1998) 252.